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ScienceDirect
Physica B 385–386 (2006) 700–702
PHYSICA B
www.elsevier.com/locate/physb

Structure of confined polymer thin films subject to shear

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Abstract

Using neutron reflectivity and the newly developed Shear Confinement Cell (SCC), we have directly quantified the density distribution of opposing neutral polymer brushes confined between parallel plates in good solvent conditions. With an average separation between the plates of approximately 1000 Å, our measurements show that the density profile in the overlap region between opposing polymer brushes flattens consistent with predictions from molecular dynamics simulations. A significant increase in density at the anchoring surfaces due to compression of the brush layers is observed. This compression or collapse of the brushes in restricted geometries strongly suggests that high-density brushes do not interpenetrate significantly in good solvent conditions. In addition, for the first time, we have measured the effects of an applied shear stress on the sample. We find that for neutral brushes, shear creates a totally new disentangled structure which surprisingly relaxes only after a time span of a few weeks.

PACS: 81.05.Lg; 82.35.Jk; 82.56.Na; 83.80.Uv; 83.85.Hf

Keywords: Neutron reflectometry; Polymers; Shear; Confinement

Polymer molecules at solid or fluid interfaces have an enormous spectrum of applications and functions in a wide variety of technologies. For example, they provide a mechanism to impart steric stabilization of colloidal dispersions, are used as protective coatings (including mechanical protection of solids against friction and wear), and are used to modulate dispersion properties (such as rheology) under a variety of processing conditions [1]. They can be designed to either promote adhesion (e.g. epoxies and glues) or they can be used to prevent sticking (such as Teflon-coated metal surfaces). In the same manner, proteins, which are natural biopolymers, govern the interactions between and functions of biological cell surfaces.

Knowledge of the conformations that adsorbed or terminally anchored chain molecules adopt when subjected to confinement and solvent flow is essential for predicting the interaction forces, and tribological, and rheological properties in thin-film technologies [2]. Theoretical [2] and modeling [3–5] investigations have been performed on polymers chemically or physically tethered to surfaces.

When densely packed polymers attached to a substrate are placed in a good solvent (for the unbound end of the polymer), the polymer free-energy consists of a competition between the osmotic forces which want the chains to dissolve in solution and the energy cost of stretching the coiled chain. The resulting carpet-like molecular structure is referred as a polymer brush. One of the characteristic properties calculated for these systems is the polymer segment density profile normal to the surface.

We have focused our studies on characterizing the structure of high-density polymer brushes formed by spin coating 50:50 polystyrene-poly-2-vinlypyridine diblocks (PS-P2VP MW = 122 k, polydispersity = 1.1, fraction P2VP = 0.51) [6,7]. The P2VP portion of the diblock is hydrogenated while the PS portion can be either hydrogenated or deuterated to take advantage of contrast labeling. Static results with hydrogenated PS-P2VP layers are reported here. Uniform polymer thin-films were

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doi:10.1016/j.physb.2006.05.297

prepared by spin coating [6,7] at 2000 rpm for 30 s on dry, ultra-clean sapphire substrates in a clean room environment. The sapphire substrates were precleaned in acetone, isopropanol, dried, and then cleaned for 10–20 min in 70:30 sulfuric acid:hydrogen peroxide at 100 °C. Afterwards, the substrates were cooled to less than 50 °C prior to rinsing with copious deionized water (18 MΩ cm) and dried using clean nitrogen. The spin coating solution was 6.0 mg/ml PS-P2VP in toluene. The polymer was dissolved in solution with continuous stirring and prepared at least 24 h in advance. Just prior to use, the solution was filtered a minimum of 3 times through 0.45 μm PTFE filters. The spin-coated polymer layers prepared in this manner were about 200 Å thick as determined by ellipsometry and only films with zero or few holes were used. After spin coating, the polymer thin-films were annealed under vacuum at 180 °C for 24 h. The substrates were then cooled to room temperature before removal from the vacuum oven. The glass transition temperature for both polymers is just over 100 °C [8]. P2VP prefers to wet the [9] sapphire (oxide) surface while PS segregates to the air interface. After annealing, an equilibrium alignment of lamellae parallel to the substrate occurs due to preferential surface wetting and the incompatibility of the PS and P2VP blocks.

Two substrates were coated as described above and then placed in contact. The substrates were then put into the confinement cell [10] shown schematically in Fig. 1. Good solvent for the PS segment (deuterated toluene) was wicked into the space between the coated blocks and neutron reflectivity measurements were performed [11] on the NG-7 reflectometer at the NIST Center for Neutron Research and the SPEAR reflectometer at LANSCE. A typical measurement for the solvated brushes with a fit to the data is shown in Fig. 2. The resulting PS volume fraction profiles for brushes at plate separations of 1175 and 850 Å are plotted in Fig. 3.

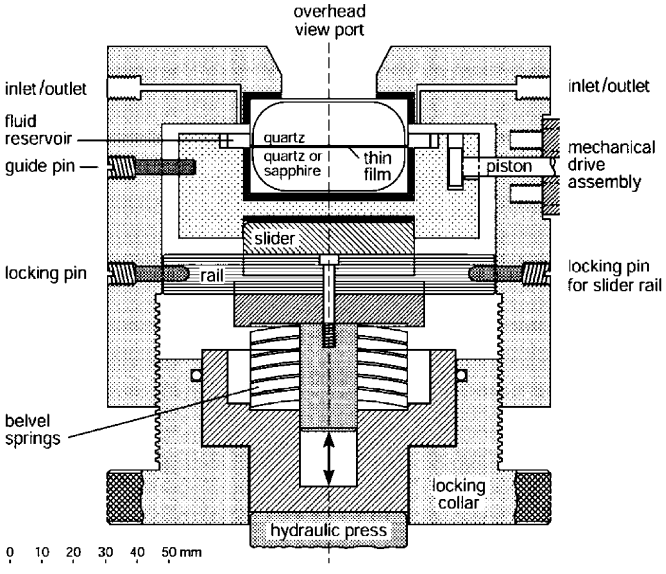

Fig. 1. Schematic design of the shear/confinement cell.

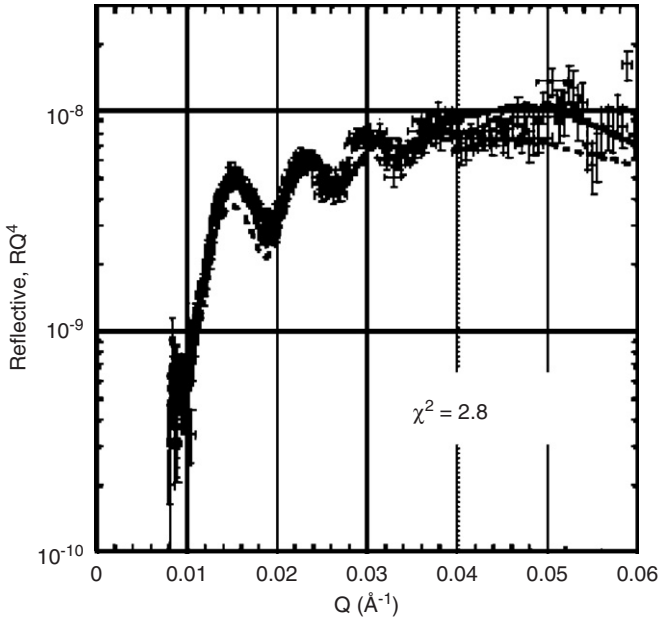

Fig. 2. Reflectivity profile for a plate separation of ~850 Å. The solid curve is a fit to the data with a parabola plus a flat region representing the PS. The dashed curve is a fit ($\chi^2 = 4.3$) to the data based on a single flat density profile for the PS.

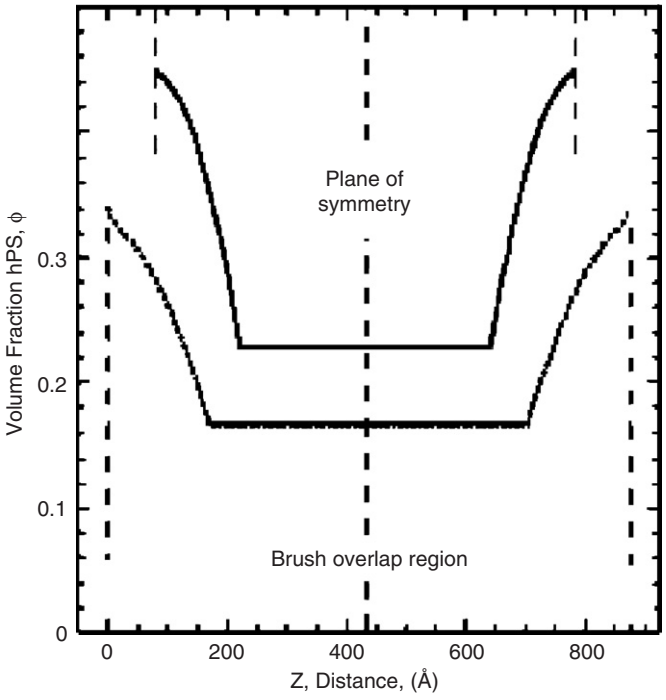

Fig. 3. Volume fraction profiles of the PS portion of the brush for the 1175 Å (lower curve) and 850 Å (upper curve) inter-substrate separation. There is significant confinement of the opposing polymer brush layers causing the density of overlap region to increase and flatten [3–5]. At the greater level of confinement, the density of PS portion of the diblock further increases at the P2VPsubstrate surface.

An identical form for the scattering length density (SLD) profile was utilized for both the 850 and the 1175 Å gap consisting of a parabola and a flat gap to describe the PS

block SLD [11]. The SLD of the parabola used to model the PS brushes and the gap SLD were allowed to vary in order to accommodate the squeezing out of d-Toluene from between the substrates and changes in the density profile of the more confined PS brushes. A comparison of the resulting volume fraction profiles for the two different confinement levels are provided in Fig. 3. A constant amount ($\pm 2\%$) of PS was obtained as expected from conservation of mass. The ability of our simple model to fit both sets of data suggests that the model represents the physical system reasonably well.

The SCC was modified (Fig. 1) with a linear ball slide attached to one of the substrates. The ball slide is attached to a stepper motor through a rotary-to-linear gear box. When the movable substrate is driven parallel to the fixed surface at a constant velocity, the fluid between the surfaces is sheared at a constant rate.

We prepared a set of samples as described above. For the initial shear runs we used a diblock copolymer where the PS block was deuterated and it was solvated with protonated toluene. After static reflectivity measurements were run confirming that we had a good separation of the two surfaces, we applied a shear stress to the film. For the first measurement, we drove the two surfaces past each other over a distance of 5 mm and a rate of roughly 1 mm/s. The reflectivity measurements were then repeated as a function of time with the plates stationary (Fig. 4). Amazingly, there was a large change in the reflectivity curve after the motion. This change has a very long relaxation time of several days. Measurements were repeated periodically over a few days. Only after several days did the curve resemble the unsheared version. These are the first measurements on a molecular length scale showing structural changes of a polymer as a function of shear in a good solvent.

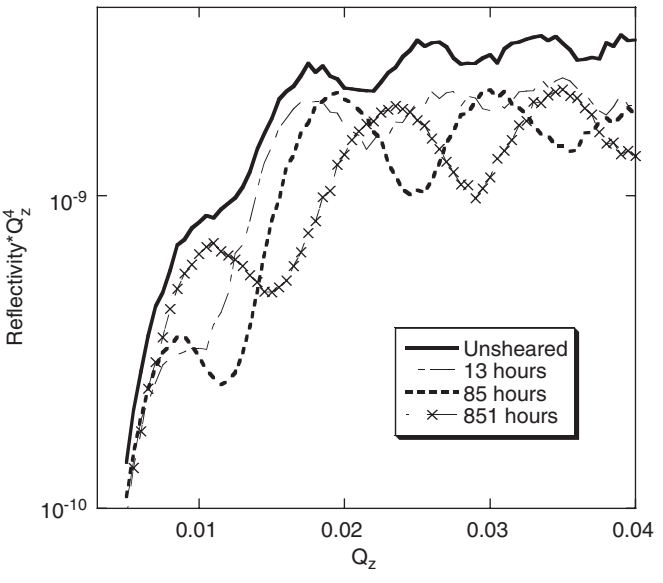

Fig. 4. Neutron reflectivity measurements of shear/confined PS-PVP diblock. The data was first measured without shearing in a good solvent. Then the sample was sheared and the measurements repeated. Several days after the shear was applied, the profiles returned to the original data.

Qualitatively, the data in Fig. 4 show a shift of the interference fringes to larger separations of Q_z in the post-shearing data versus the unsheared data. This implies that the gap thickness has decreased. Perhaps more interesting is that the post-shearing data not only shows this shift, but also has more visible fringes implying that the two surfaces are better aligned [11]. We are continuing to analyze this data to extract the details of this time-dependent structure. Also, we plan to repeat the measurements with different contrasts using deuterated toluene as the solvent.

In conclusion, we have utilized neutron reflectivity to determine the density distribution of opposing polymer brush layers as a function of confinement. The resultant volume fraction profiles are consistent with predictions from molecular dynamics simulations and mean field theory showing a flattening in the overlap region. However, a significant increase in concentration at the di-block interface was also evident, which had not been previously suggested, and indicates that compression of the brushes is more dominant than interdigitation. In addition, we have measured for the first time the reflectivity from a polymer in confinement and subject to shear. Further investigation and analysis are being performed to understand the nature of the sheared structure and its long relaxation time.

Oak Ridge National Laboratory is managed for the United States Department of Energy, Office of Basic Energy Sciences- Materials Science, (DOE) under contract DE-AC05-00OR22725 with UT-Battelle LLC. The Manuel Lujan Jr., Neutron Scattering Center is a national user facility funded by DOE under contract number W-7405-ENG-36 with the University of California. Partial support for this work came from Grant no. 41489-AC7 from the American Chemical Society Petroleum Research Fund (ACS-PRF). We also acknowledge the support of the National Institute of Standards and Technology, US Department of Commerce, in providing neutron research facilities for this work.

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